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The objective of this project is to investigate the epitaxial growth of device quality III-V semiconductor films by the free electron laser-induced epitaxial growth technique at low temperatures. Efforts during the past year has been focused to the homo- and heteroepitaxial growth and characterization of gallium arsenide (GaAs) films on GaAs and silicon (Si) substrates by laser-induced metalorganic chemical vapor deposition (LIMOCVD). ArF excimer laser (193 nm) was used before the free electron laser is available. The reaction between trimethylgallium and arsine in hydrogen under reduced pressure was used for the epitaxial growth of GaAs. Homoepitaxial GaAs films deposited by LIMOCVD at 425°-500°C are similar to conventional homoepitaxial GaAs films (at 700°C) in properties. Heteroepitaxial GaAs films on Si substrates of (100) orientation have been deposited at 500°C by LIMOCVD with emphasis on the cleanliness of the substrate surface. Transmission electron microscopy and Raman spectra indicated that the heteroepitaxial GaAs films are presumably of a (111) orientation and that their crystalline perfection is superior to those deposited by other techniques.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

SUMMARY

This is the Second Annual Report of a research project "Laser Induced Chemical Vapor Epitaxial Growth of Gallium Arsenide Films" sponsored by the Free Electron Laser Material Science Program of the SDIO Technology Application Programs under contract number ONR N00014-86-K-0740. The objective of this project is to investigate the epitaxial growth of device quality III-V semiconductor films by the free electron laser-induced epitaxial growth technique at temperatures considerably below the temperature required in the conventional deposition process.

Efforts during the past year has been focused to the homo- and hetero-epitaxial growth of gallium arsenide (GaAs) films by laser-induced metal-organic chemical vapor deposition (LICVD) and the characterization of the properties of the epitaxial films. ArF excimer laser (193 nm) was used before the free electron laser is available. The reaction between trimethylgallium (TMG) and arsine (AsH_3) in a hydrogen atmosphere under reduced pressure was used for the epitaxial growth of GaAs. Silicon (Si) wafers of (100) orientation were used as substrates for the heteroepitaxial growth of GaAs. The important process parameters are: the substrate surface cleanliness, substrate temperature, composition and flow rate of the reaction mixture, pressure in the reaction chamber, and the pulse energy and pulse rate of the laser.

Homoepitaxial GaAs films have been deposited under a wide range of process parameters: substrate temperatures of 425°-500°C, laser pulse energy of 80-100 mJ, laser pulse rate of 60-80 Hz, AsH_3/TMG molar ratio of 20 or higher, and pressure in the deposition reactor of 10-30 Torr. The substrate temperature is significantly lower than that used in conventional MOCVD process. Transmission electron microscopy (TEM) confirmed the good structural perfection of the interface region and the grown layer. The dopant profile and carrier mobility measurements indicated that GaAs films deposited by LIMOCVD are very similar to those deposited by the conventional MOCVD technique.

The heteroepitaxial of GaAs films on Si substrates of (100) orientation have also been deposited at 500°C by LIMOCVD with particular emphasis on the cleanliness of the substrate surface. It was also essential to use lower deposition rate than the homoepitaxial growth process. Electroreflectance, TEM, and Raman spectroscopic techniques indicated that the heteroepitaxial GaAs film deposited by LIMOCVD is presumably of a (111) orientation and that its crystalline perfection is superior to those deposited by other techniques. For example, the density of threading dislocations at the interface region is negligible and stacking faults appear to be the major defect in the GaAs film.

Section 1.0

INTRODUCTION

This is the Second Annual Report of a research project "Laser Induced Chemical Vapor Epitaxial Growth of Gallium Arsenide Films" sponsored by the Free Electron Laser Material Science Program of the SDIO Technolgy Application Programs under contract number ONR N00014-86-K-0740. The objective of this project is to investigate the epitaxial growth of device quality III-V semiconductor films by the free electron laser-induced epitaxial growth technique at temperatures considerably below the temperature required in the conventional deposition process.

III-V compound semiconductors have become increasingly important in electronic devices and circuits. Gallium arsenide (GaAs), indium phosphide (InP), and many III-V ternary and quaternary alloys have unique applications in radiation detectors, solid-state lasers, microwave, electro-optic, and gigabit-rate logic devices. The homo- and hetero- epitaxial growth techniques are essential to provide device-quality III-V compounds and their alloys needed for the majority of these devices. Of all the alternative epitaxial techniques, metalorganic chemical vapor deposition (MOCVD) has demonstrated the capability to grow the widest variety of III-V materials with excellent doping and thickness control. Monolayer thickness and transition [1,2] are possible. Very low thresholds in $Al_xGa_{1-x}As/GaAs$ lasers [3] and uniform emission wavelength in $Ga_{1-x}In_xP_yAs_{1-y}$ lasers [4] have also been demonstrated. The process is capable of growing several different III-V alloy systems in the same apparatus, in any sequence, during a single deposition process. For example, abrupt heterojunction structures, such as $GaP_yAs_{1-y}/Ga_{1-x}In_xAs$, has only be prepared by the MOCVD process.

In the conventional MOCVD process, the deposition temperatures are usually in the range of 600-800°C. The advantages of the epitaxial growth of GaAs and other III-V compounds at lower temperatures by the MOCVD technique are well recognized. The contamination and interdiffusion can be minimized in multilayer device structures, the process-induced defects due to thermal stress can be reduced, and the processing flexibility, such as the epitaxial growth of GaAs and InP on Si substrates can open up many avenues in device fabrication. The major advantage of this technology is the possibility to merge the high electron mobility of GaAs and InP with the high-level integration capabilities of Si. A new breed of integrated circuits combining Si-based digital circuits with GaAs optoelectronics can be achieved for light-based interconnections. For example, GaAs/$Al_xGa_{1-x}As$ optoelectronic interface units could provide high-data-rate optical link to replace wire interconnects between Si VLSI subsystems. Similarly, the monolithic integration of GaAs microwave devices and silicon integrated circuits has numerous applications. In the near term, the GaAs on Si technology can utilize the low-cost, high mechanical strength Si substrates instead of expensive, brittle GaAs wafers. Thus, GaAs films can reach the size of current Si wafers (5 to 8" in diameter), while the bulk GaAs wafers have diameters of only 2 to 3". GaAs devices would also benefit from the higher thermal conductivity of silicon substrate.

The major difficulties involved in obtaining device quality GaAs on Si are the mismatches in lattice parametrs (GaAs: 5.654 Å; Si: 5.431 Å) and thermal expansion coefficients (GaAs: 6.8×10^{-6} °C^{-1}; Si: 2.6×10^{-6} °C^{-1}) between GaAs and Si. As a result, epitaxial GaAs layers on Si substrates have high dislocation densities, anti-phase domains, and microcracks. The anti-phase domains has been eliminated by using silicon substrates 3° to 4°

off the (100) toward a [011] or a [111] direction [5,6]. The dislocation densities can be reduced by using the germanium interlayer, the superlattice buffer layer, or the combination of low and high processing temperatures. However, the dislocation densities cannot be reduced to lower than 10^6 cm^{-2}. Further, the microcracks generated in the epitaxial GaAs layer grown by conventinal MOCVD always develop when the thickness of the GaAs layer is more than 3 μm due to the use of high deposition temperatures. Therefore, the epitaxial growth of GaAs on Si at reduced growth temperature with reasonable growth rates is desirable to produce low defect density and crack-free films.

The use of high power ultraviolet radiation and tunable wavelength FEL offers a novel approach to the preparation of device-quality semiconductor films of controlled electrical and structural properties. The excitation of reaction species to higher electronic states by the FEL will enable the use of considerably lower temperatures for the preparation and crystal growth of semiconductors. The approaches used in this program include (a) the use of an excimer laser before the FEL is available since essentially all source materials for the MOCVD of III-V semiconductors absorb radiation in the ultraviolet region, (b) the homo- and hetero-epitaxial growth of GaAs, $Al_xGa_{1-x}As$ on single crystalline GaAs and Si substrates by using the laser-induced MOCVD process at deposition temperatures considerably below the temperature required in conventional MOCVD, and (c) the characterization of structural and electronic properties of the deposited films in correlation with the deposition parameters.

Major efforts during this reporting period have been directed to (a) the deposition of homoepitaxial gallium arsenide films by laser-induced

MOCVD, (b) the characterization of the electrical properties of homoepitaxial GaAs films as a function of deposition parameters, (c) the deposition of heteroepitaxial GaAs films on single crystalline Si substrates, and (d) the characterization of the heteroepitaxial GaAs films on Si substrates. Homoepitaxial growth of gallium arsenide films has been achieved at temperatures as low as 425°C and heteroepitaxial growth at 450°-500° by laser-induced MOCVD. This capability of low temperature epitaxial growth is expected to have wide industrial applications. A paper entitled "ArF Excimer Laser-Induced Epitaxial Growth of Gallium Arsenide Films," has been published in Applied Physics Letter and is attached as Appendix A. Another paper entitled "The Heteroepitaxial Growth of GaAs films on Si by Laser-Induced MOCVD," was presented at the Spring Meeting of the Materials Research Society and the paper will be published in the proceedings of the symposium. The experimental procedures and results are discussed in the following sections.

Section 2.0

LASER-INDUCED MOCVD

The use of an excimer laser to excite the reaction species to higher electronic states is an attractive approach to the low temperature epitaxial growth of III-V compounds. Homoepitaxial growth of InP films using ArF (193 nm) excimer laser-induced photochemical decomposition of $(CH_3)_3In$ and $(CH_3)_3P$ at 500°C has been reported [7]. Similar approaches; however, have produced only polycrystalline GaAs films at 400°C using ArF laser stimulated decomposition of $(CH_3)_3Ga$ (TMG) and $(CH_3)_3As$ [8]. The homoepitaxial growth of GaAs and heteroepitaxial growth of GaAs on Si using laser-induced MOCVD are investigated in this program.

A Lumonics Model HE-460-SM-A ArF laser of 193 nm was used for the excitation of the reaction species in the MOCVD process. This laser is capable of operating at constant power under microprocessor control. The maximum average power, maximum pulse energy, pulse rate for maximum average power, and pulse duration are 25 watts, 400 mJ, 80 Hz, and 10-12 ns, respectively. The output beam cross-sectional area was 8 x 33 mm, and no homogenizer was used. The laser-induced deposition was carried out under reduced pressure to minimize the gas phase nucleation. The MOCVD process and the deposition system are briefly discussed in this section.

2.1 MOCVD PROCESS

The MOCVD process involves the reaction of gaseous mixtures of one or more hydride and one or more metalorganic compound on the substrate surface. The metalorganics of interest are typically liquids at room temperature with relatively high vapor pressures and can be readily transported into the reactor by bubbling a carrier gas, such as H_2, through the liquid source.

The hydrides of interest are gases at room temperature and are generally used as dilute mixtures in a H_2 matrix. The reaction between the metal-organic compound and the hydride is usually carried out in a H_2 atmosphere in a gas flow reactor. Deposition temperatures are in the range of 600-800°C. The MOCVD growth of GaAs involves the chemical reaction between trimethylgallium (TMG) (b.p. 55.7°C) and arsine, AsH_3, in a hydrogen atmosphere:

$$(CH_3)_3Ga(g) + AsH_3(g) \xrightarrow[700°C]{H_2} GaAs(s) + 3CH_4(g)$$

Similar reactions are used for the growth of other binary, ternary, and quaternary compound semiconductors. The growth of $Al_xGa_{1-x}As$ can be carried out by substituting part of the TMG with trimethylaluminum (TMA):

$$(1-x)[(CH_3)_3Ga](g) + x[(CH_3)_3Al](g) + AsH_3(g) \xrightarrow[700°C]{H_2} Al_xGa_{1-x}As(s) + 3CH_4(g)$$

The composition of the solid solution, x, is directly related to the relative initial partial pressures of TMG and TMA in the vapor phase. This is also true for many quaternary III-V alloys grown by MOCVD, for example, $Ga_{1-x}Al_xAs_{1-y}P_y$. The doping in the grown material can be accomplished by using diethylzinc (DEZ) or bis-cyclopentadienyl magnesium as the p-type dopant and H_2Se or SiH_4 as the n-type dopant.

In the conventional MOCVD, the substrates are usually placed on a silicon carbide coated graphite susceptor in a fused silica reaction tube, and the susceptor heated externally by an rf generator. This cold-wall reactor avoids undesirable deposition on the wall of the reactor and homogeneous nucleation through reactions in the gas phase. The conventional MOCVD can either be carried out under atmospheric or reduced pressure. The

advantage of using reduced pressure is to avoid turbulent flow dynamics and to increase deposition efficiency.

2.2 DEPOSITION SYSTEM FOR LASER-INDUCED MOCVD

The deposition chamber used for the laser-induced epitaxial growth of GaAs was made of fused silica with a Suprasil II window, as shown schematically in Fig. 2-1. The chamber was equipped with gas inlet and outlet tubes, purging gas for the window, and a thermocouple insert. The substrate was heated by a quartz halogen lamp and the temperature of a thermocouple was in direct contact with the surface of the substrate to control and monitor its temperature. The direction of the laser beam was perpendicular to the substrate surface. The low pressure control system consisted of a microprocessor operated throttle valve, a Baratron gauge, and a vacuum pump. The exhaust gas from the reactor, before entering the throttle valve, was passed through a cracking furnace and a liquid nitrogen trap to ensure the complete decomposition and removal of all unreacted species. The system is capable of controlling the pressure in the reaction chamber down to 1 Torr or less. The flow of the reaction mixture through the reaction chamber was measured by mass flow controllers operated by a HP 85B computer.

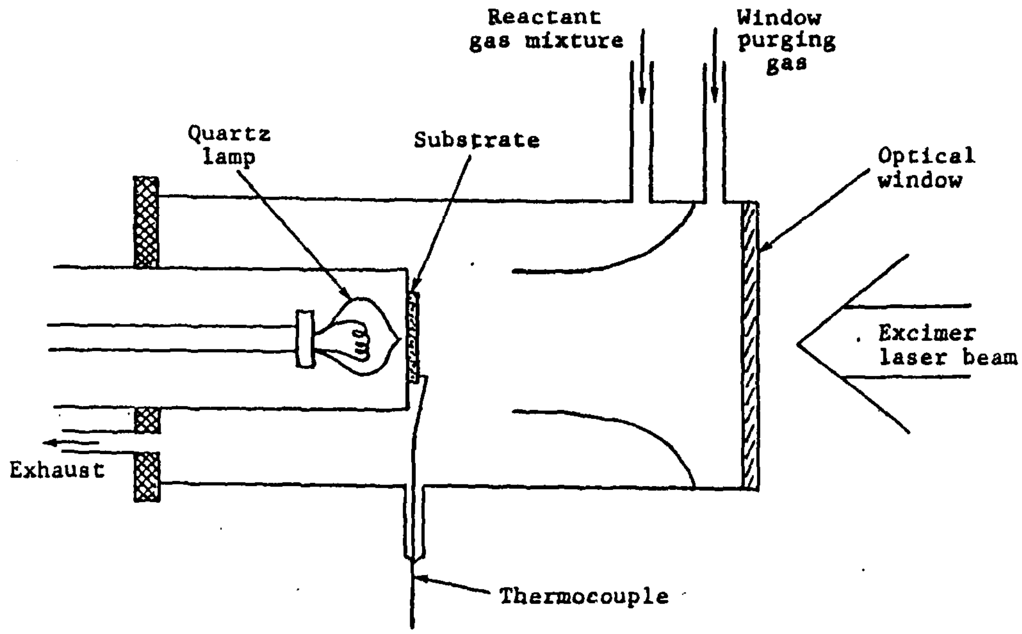

Figure 2-1 Schematic diagram of the reaction chamber.

Section 3.0

HOMOEPITAXIAL GROWTH OF GaAs FILMS BY LASER INDUCED MOCVD

3.1 DEPOSITION OF HOMOEPITAXIAL GaAs FILMS

The homoepitaxial growth of GaAs films was carried out by the laser-induced reaction between TMG and AsH_3, and hydrogen was used as the diluent and window purging gas [9]. The important process parameters are: the substrate surface cleanliness, substrate temperature, composition and flow rate of the reaction mixture, pressure in the reaction chamber, and the pulse energy and pulse rate of the laser. The importance of the cleanliness of the substrate surface in the epitaxial technology is well established.

Single crystalline n-type GaAs wafers of (100) orientation were used as the substrates. After routine etching and cleaning, the substrate was placed in the reaction chamber, and the chamber was evacuated and purged with hydrogen. The evacuation and purging were repeated several times and the chamber was reevacuated to less than 0.1 Torr. The surface of the substrate was perpendicular to the direction of the laser beam. Hydrogen was introduced to maintain the pressure in the chamber at 10-30 Torr under continuous evacuation. Prior to the deposition process, the substrate was etched in-situ at 500°C by laser irradiation at a laser pulse energy of 90-95 mJ. Under these conditions, the etching caused no damage to the substrate by examination under a scanning electron microscope (SEM). Deposition experiments were carried out over a wide range of process parameters: substrate temperature of 425°-500°C, laser pulse energy of 50-100 mJ, laser pulse rate of 40-80 Hz, AsH_3/TMG molar ratio of 4-30, and pressure of 10-30 Torr. The optimization of the deposition parameters were carried out in conjunction with the characterization processes. The

structural and electrical properties of the deposited films were determined as functions of the deposition parameters.

In order to verify that the deposition was initiated from the excitation of the reaction species by the laser irradiation, homoepitaxial growth experiments have been carried out without laser irradiation under otherwise the same deposition conditions. No deposition was observed in all experiments even at temperatures up to 600°C.

3.2 CHARACTERIZATION OF HOMOEPITAXIAL GaAs FILMS

The structural and electrical properties of the deposited homoepitaxial films were characterized by using scanning electron microscopy (SEM), transmission electron microscopy (TEM), electrochemical carrier concentration profile, secondary ion mass spectrometry (SIMS), and Hall measurements.

Specular and mirror smooth films have been deposited at AsH_3/TMG molar ratios of 10 or higher in the temperature range of 425-500°C, laser pulse energies of 80-100 mJ, and pulse rates of 60-80 Hz. The as-grown and chemically etched surfaces exhibited no structural features when examined under a SEM. However, when the deposition was carried out at lower AsH_3/TMG molar ratios, the films had hazy appearance, particularly after chemical etching, and SEM examinations indicated the presence of polycrystalline inclusions. Two samples prepared at 450°C and 500°C using a mole fraction of TMG of 1.6×10^{-4}, AsH_3/TMG molar ratio of 20, laser pulse energy of 95 mJ, and laser pulse rate of 70 Hz have been examined by using TEM performed on [011] cross section. The sample prepared at 500°C showed no defects at the interface region, and the substrate/film interface was not visible. The sample prepared at 450°C also showed no defects; however, the interface was distinguishable as shown in Fig. 3.1.

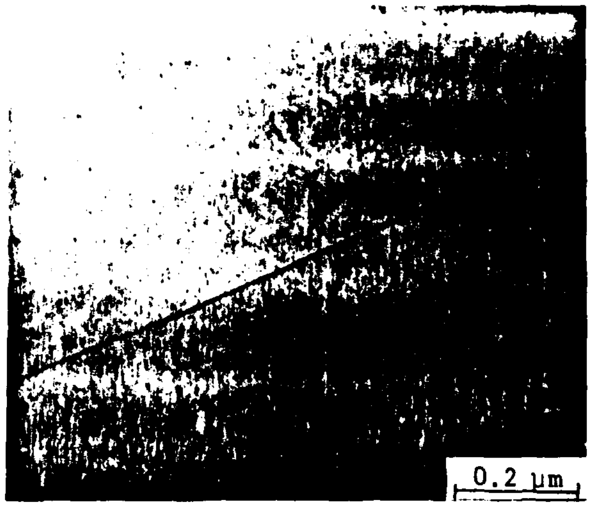

Figure 3.1 Transmission electron micrograph of a cross-sectional surface of a GaAs film deposited at 450°C for 10 mins. The deposition conditions: mole fraction of TMG, 1.6×10^{-4}; AsH_3/TMG molar ratio, 20; laser pulse energy, 95 mJ; laser pulse rate, 70 Hz.

The deposition rate was determined by direct measurement of the angle polished and etched cross-sectional surface of the deposited film under SEM and by using the Polaron Model 4200 depth profiler. The deposition rate varied from higher than 0.1 μm/min at substrate temperature of 500°C to about 0.02 μm/min at 425°C when a mole fraction of TMG of 1.6×10^{-4}, AsH_3/TMG molar ratio of 20, laser pulse energy of 95 mJ, and laser pulse rate of 70 Hz were used.

The carrier concentration profile in laser-induced homoepitaxial GaAs films was determined by using the Polaron Model 4200 depth profiler. An example is shown in Fig. 3.2 where a p-type epitaxial film of about 1 μm thickness with a carrier concentration of about 10^{17} cm^{-3} was deposited on an n-type substrate (carrier concentration ~ 10^{17} cm^{-3}) at 500°C. Thus, the laser-induced MOCVD can provide epitaxial films of uniform carrier concentration in the growth direction.

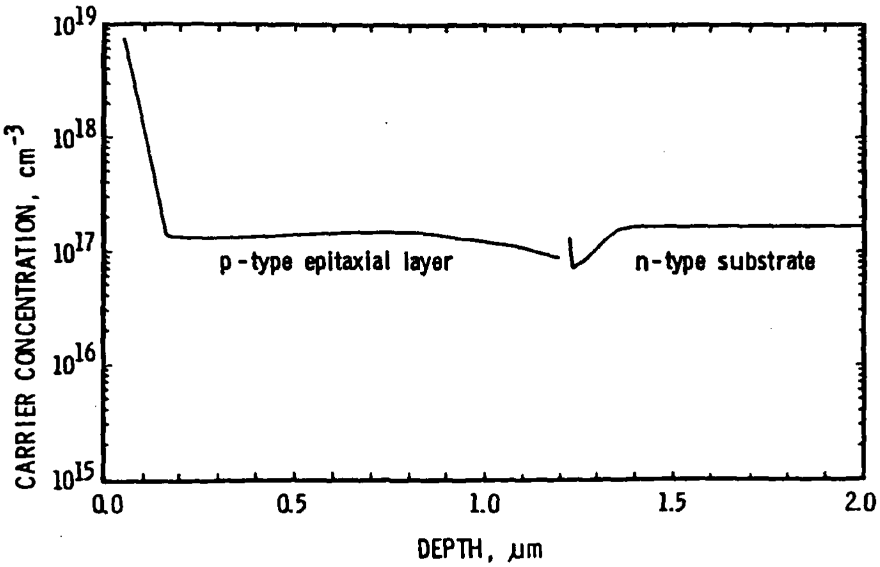

Figure 3.2. The hole concentration profile of a p-type epitaxial GaAs film deposited on n-type substrate (n ~ 10^{17} cm^{-3}). The deposition conditions: substrate temperature, 500°C; mole fraction of of TMG, 1.6 x 10^{-4}; AsH_3/TMG molar ratio, 20; laser pulse energy, 95 mJ; laser pulse rate, 70 Hz.

The carrier concentration and mobility of the deposited film were determined by the van der Pauw's technique, since the deposited film and the substrates were of opposite conductivity type. Au-Zn alloy was used as ohmic contacts to the p-type epitaxial films. At a given substrate temperature, the carrier concentration depends strongly on the AsH_3/TMG molar ratio in the reactant mixture. For example, the hole concentration varies from (1-2) x 10^{18} cm^{-3} to (3-4) x 10^{16} cm^{-3} as the AsH_3/TMG molar ratio increased from 10 to 30 at a substrate temperature of 500°C, as shown in Fig. 3.3. The carbon content in GaAs films deposited at 500°C was determined by the SIMS technique to be 4 x 10^{17} to 2 x 10^{18} cm^{-3}. While the carbon concentration is higher in GaAs films deposited at low AsH_3/TMG molar ratios, the

carbon content in the films cannot be readily correlated with the carrier concentration. The concentration of oxygen in all films deposited at 500°C was found to be below the detection limit of the SIMS technique, 2×10^{18} cm^{-3}. The hole concentration in epitaxial GaAs films depends on substrate temperature, and the dependence is more pronounced at low substrate temperatures, as shown in Fig. 3.4. Using a fixed AsH_3/TMG molar ratio of 20, the hole concentration varied from 5×10^{16} cm^{-3} at a substrate temperature of 425°C to $(2-3) \times 10^{17}$ cm^{-3} at 500°C. This could be due to the higher carbon incorporation at higher deposition temperatures. The hole mobilities are in the range of (150-200) cm^2/V-sec. Thus, the properties of the homoepitaxial GaAs films deposited at low temperatures by the ArF excimer laser-induced MOCVD are very similar to those deposited by the conventional MOCVD technique.

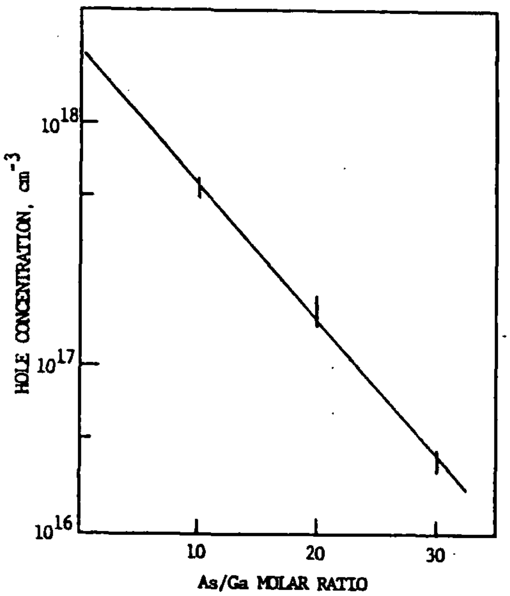

Figure 3.3 **The hole concentration in the epitaxial GaAs films deposited at 500°C as function of AsH_3/ TMG ratio. Other deposition conditions are the same as those shown in Fig. 3.1.**

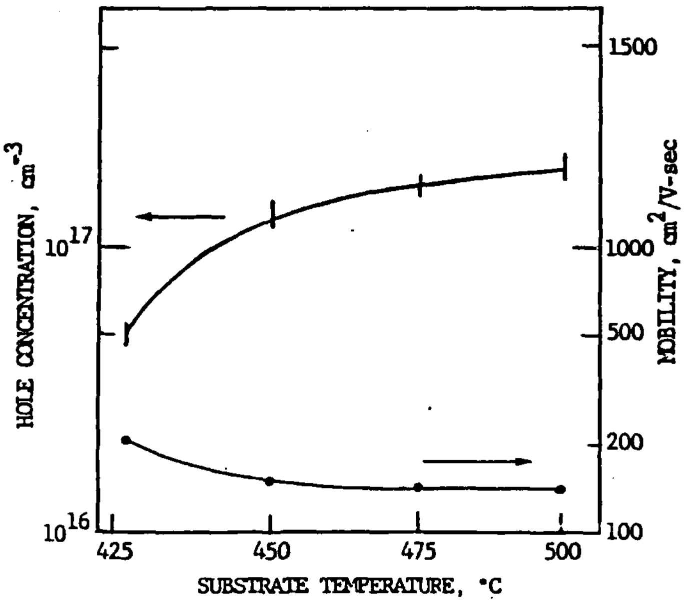

Figure 3.4 The hole concentration and mobility in epitaxial GaAs films as a function of substrate temperature. The deposition conditions are the same as those shown in Fig. 3.1.

Section 4.0

DEPOSITION AND CHARACTERIZATION OF HETEROEPITAXIAL GaAs FILMS

In view of the broad interest of device-quality heteroepitaxial GaAs films on Si and the major difficulties involved in obtaining device quality heteroepitaxial films by conventional deposition techniques, the heteroepitaxial growth of GaAs films on single crystalline Si substrates was carried out by the laser induced MOCVD. Prior to the heteroepitaxial growth of GaAs films on Si, the heteroepitaxial growth of GaAs films on single crystalline germanium (Ge) substrates were carried out since Ge is an ideal substrate for the deposition of GaAs films. Gallium arsenide and germanium have the same crystal symmetry and similar lattice parameter (GaAs: 5.654 Å; Ge: 5.658 Å) and thermal expansion coefficient (GaAs: 6.8×10^{-6} °C^{-1}; Ge: 5.92×10^{-6} °C^{-1}). Thin film GaAs solar cells have been prepared on Ge coated silicon substrates to minimize the stress between GaAs and Si [10]. The heteroepitaxial growth of GaAs films on Ge and Si substrates by laser-induced MOCVD has been investigated in this program and the results are summarized below.

4.1 DEPOSITION AND CHARACTERIZATION OF HETEROEPITAXIAL GaAs FILMS ON Ge SUBSTRATES

Single crystalline Ge wafers of (100) orientation were used as the substrates. They were cleaned and etched in CP4 (15 HF, 25 HNO_3, 15 $HC_2H_3O_2$) for 2 min, followed by thorough rinsing. Similar to the homoepitaxial growth of GaAs, the surface of Ge substrates was also cleaned in-situ by laser irradiation. The process parameters required for the growth of device-quality heteroepitaxial GaAs on Ge substrates are similar to those of homoepitaxial GaAs films. For example, using a substrate temperature of 500°C,

laser pulse energy of 87 mJ, laser pulse rate of 70 Hz, mole fraction of TMG of 1.6×10^{-4}, and AsH_3/TMG molar ratio of 20, heteroepitaxial GaAs films with specular and mirror smooth surface have been obtained. Chemical etching and SEM examinations confirmed the good structural perfection of these films. The deposition rate was about 0.1 μm/min and the deposited film was also p-type with a hole concentration of about 1.5×10^{17} cm^{-3} as determined by the Polaron electrochemical depth profiler. The properties of heteroepitaxial GaAs films on Ge substrates are very similar to those of homoepitaxial GaAs films grown under the same conditions.

4.2 DEPOSITION AND CHARACTERIZATION OF HETEROEPITAXIAL GaAs FILMS ON Si SUBSTRATES

Due to the mismatches in lattice parameters and thermal expansion coefficients, the major problem associated with the heteroepitaxial growth of GaAs on Si is the formation of high dislocation densities and microcracks in the deposited GaAs films. The reduction of dislocation densities in heteroepitaxial GaAs films on Si substrates has been investigated using (1) the silicon substrates of {100} orientation tilted 3° to 4° toward a [110] direction [11,12], (2) the interupted growth [11,13], (3) the germanium interlayer [10], (4) the thermal annealing [14,15], (5) the combination of low and high processing temperatures [6 ,16], and (6) the superlattice buffer layer [17,18]. The most simple and relatively successful approach is the use of 100 silicon substrates tilted toward a [110] direction. The heteroepitaxial GaAs films on such substrates had fewer threading dislocations than those grown on the {100} surface. Further, two types of misfit dislocations have been found to be present in the GaAs/Si interface: one with a Burgers vector parallel to the {100} interface (type I), and the

other with a Burgers vector inclined from the {100} interface by 45° (type II). The tilting of the substrate surface significantly reduced the fraction of type II dislocations in the misfit dislocation configuration. However, GaAs films of several micrometers in thickness are required to achieve low defect density near the surface. The use of such a thick layer generates defects due to the difference in thermal expansion coefficients, and microcracks always develop in thick heteroepitaxial GaAs films during the cooling process [6 ,10].

Many GaAs devices have been demonstrated using heteroepitaxial GaAs films on Si with dislocation densities of 10^5-10^6 cm^{-2}. They include the metal-semiconductor field-effect transistors [19], bipolar transistors [20], AlGaAs/GaAs multiple quantum well lasers [21], and integrated circuits [22]. While the characteristics of the majority carrier devices are reasonable, the minority carrier devices have inferior properties. The improvement on the quality of the heteroepitaxial GaAs films on Si is necessary for the success of this important technology.

The use of reduced temperature growth is highly desirable in view of the thermal stress-induced defects and microcracks associated with the heteroepitaxial growth of III-V compounds on Si. The heteroepitaxial growth of GaAs films on Si substrates at low temperatures has been carried out by the laser-induced MOCVD and the properties of the deposited GaAs films characterized.

Single crystalline silicon wafers of 3° off the {100} orientation toward a [110] direction were used as the substrates. Similar to the hetero-epitaxial growth on Ge substrates, the substrates were cleaned and etched in the CP4 polishing etchant followed by thorough rinsing. The chemically processed surface of Si is always covered with a native oxide film of about

20 Å thickness. Because of its inertness, the SiO_2 film on the surface of silicon substrates is considerably more difficult to remove than the native oxides on the surface of Ge or GaAs. Since the cleanliness of the substrate surface is a most important factor affecting the structural perfection of deposited films, major efforts were focused to the in-situ cleaning of the Si surface by laser irradiation in H_2 under reduced pressure without damaging the substrate. The results of a series of experiments indicated that higher substrate temperatures (~600°C) and higher laser pulse energy (~100 mJ) were essential for the complete removal of the surface oxide. When the deposition of GaAs was carried out at a substrate temperature of 500°C using similar conditions as those used for the homoepitaxial growth of GaAs films, the deposited films always contained polycrystalline inclusions. The structural perfection of GaAs was significantly improved by reducing the growth rate through the use of lower concentration of TMG in the reactant mixture. The use of lower growth rate was particularly important during the initial stage of deposition.

The heteroepitaxial GaAs films on Si have been characterized by TEM, electroreflectance, and Raman spectroscopic techniques. The electroreflectance spectrum, measured at the Physics Department of the University of South Florida, indicated the presence of two peaks below the energy of 3.0 eV, E_o and E_1, at 1.45 eV and 2.9 eV, respectively as shown in Fig. 4.1. These energies are in good agreement with the established experimental values for GaAs (E_o = 1.436 eV, direct bandgap; E_1 = 2.915 eV, indirect bandgap). The electroreflectance peak at the energy of 2.9 eV is particularly useful in probing the uniformity of carrier density near the surface of the GaAs layer. The topographical map of the relative carrier

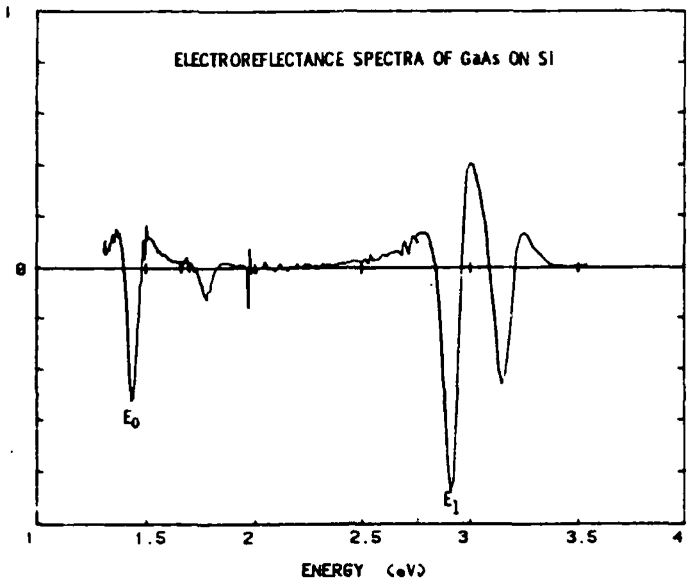

Figure 4.1 Electroreflectance spectra of a heteroepitaxial GaAs film on Si. The deposition conditions: mole fraction of TMG, 8 x 10^{-5}; AsH_3/TMG molar ratio, 20; laser pulse energy, 95 mJ; laser pulse rate, 70 Hz, deposition time, 10 mins.

density distribution on an area of 5.2 mm x 5.2 mm is shown in Fig. 4.2. The depth of penetration at this energy is about 300 Å. The carrier density is uniform except near one corner of the sample.

TEM examinations have been performed on the cross sections of two samples at the Central Research Laboratories of Texas Instruments Incorporated. While stacking faults were observed in the heteroepitaxial GaAs film near the interface, there is no apparent threading dislocations in surface region of the GaAs films of 0.15-0.2 μm thickness as demonstrated in Figure 4.3.

The Raman spectra, measured at the University of South Florida, of five different regions of a heteroepitaxial GaAs indicated that the peak of the transverse optical (TO) mode at 267 cm^{-1} is strong and the the peak of the

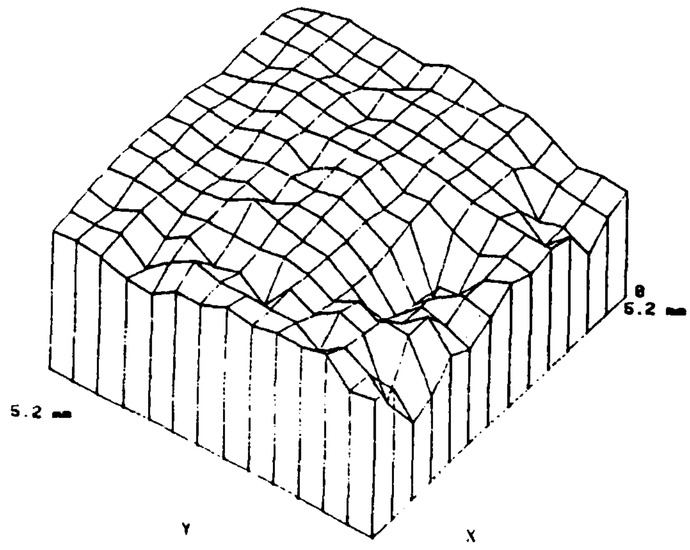

Figure 4.2 The topographical map of relative carrier density on an 5.2 mm x 5.2 mm area of a heteroepitaxial GaAs film on Si substrate. The deposition conditions are the same as those shown in Fig. 4.1.

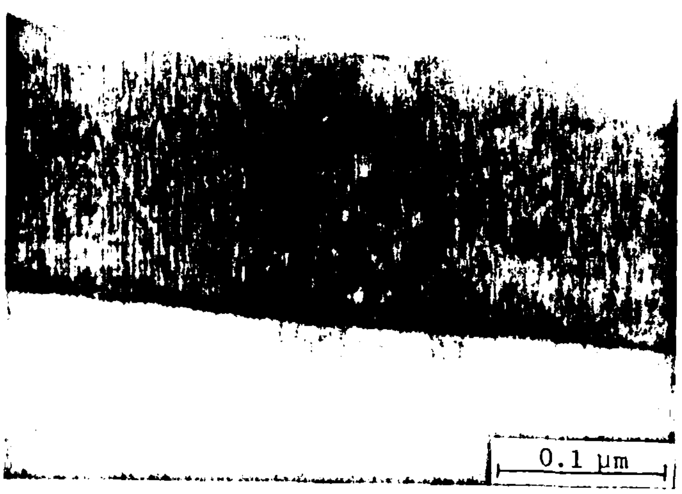

Figure 4.3 TEM of a cross-sectional surface of a heteroepitaxial GaAs film on Si. The deposition conditions are the same as those shown in Fig. 4.1.

longitudinal optical (LO) mode at 290 cm^{-1} is weaker. The Raman spectra are identical at different regions of the sample, and the spectra are very clean indicating the uniform structural perfection of the GaAs film. The selection rules of the Raman transitions for different crystallographic orientation of GaAs are shown in Table 4.1. The appearance of both TO and LO modes in Raman spectra suggested that the crystallographic orientation is more likely to be [111]. However, there is possibility that the crystallographic orientation can be [110] since the peak of the TO mode is much stronger than that of the LO mode. This is believed to be the first observation that the crystallographic orientation of heteroepitaxial GaAs film is different from the substrate. The absence of the threading dislocations, observed by TEM, is due presumably to the different crystallographic orientation between GaAs and Si, and the in-situ cleaning of the Si surface by laser irradiation is probably an important factor.

Table 4.1 Selection Rules of Raman Spectra for GaAs

Crystallographic Orientation	Transverse Mode (267 cm^{-1})	Longitudinal Mode (290 cm^{-1})
[111]	Allowed	Allowed
[110]	Allowed	Forbidden
[100]	Forbidden	Allowed

The condition of the substrate surface has been shown to affect the crystalline quality of CdTe films deposited on GaAs substrates [21]. CdTe (a = 6.48 Å) and GaAs (a = 5.654 Å) has a lattice mismatch of 14.6%. The heteroepitaxial growth of CdTe on (100) GaAs substrates by MOCVD has shown that the crystallographic orientation of CdTe films depends on the substrate

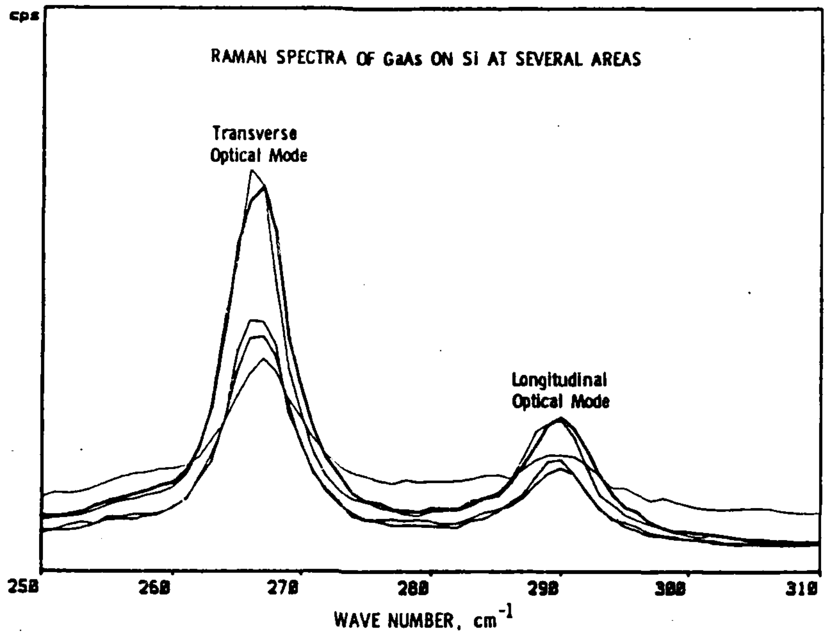

Figure 4.4 Raman spectra of a heteroepitaxial GaAs film on Si substrate. The deposition conditions are the same as those shown in Fig. 4.1.

preparation such as annealing [22]. CdTe films of (111) orientation were grown reproducibly on annealed (100) GaAs substrates whereas (100) CdTe films were obtained on unannealed (100) GaAs substrates. The (100)CdTe/(100)GaAs interface had a high defect density due to the large lattice mismatch, and high quality crystal perfection was observed at the (111)CdTe/(100)GaAs interface. The results on the heteroepitaxial growth of CdTe on GaAs substrates suggest that the absence of threading dislocations in the heteroepitaxial GaAs on Si substrates grown by laser-induced MOCVD is due presumably to the clean Si surface provided by in-situ laser irradiation. Apparently, other techniques for the cleaning of Si surface is not as effective. The results of the CdTe/GaAs system also suggests that the

heteroepitaxial GaAs film is of [111] orientation to account for the absence of threading dislocations.

On the basis of the above discussion, the results obtained so far are indeed encouraging. The heteroepitaxial growth of GaAs on Si substrates by laser-induced MOCVD and the detailed characterization of the deposited films will be continued.

Section 5.0

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